THERMODYNAMIC PROPERTIES OF GAS MIXTURES AT HIGH TEMPERATURES

BY

ALBERT EBY HERSHEY

B.S., Carnegie Institute of Technology, 1922
M.S., University of Illinois, 1926

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
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OF THE UNIVERSITY OF ILLINOIS, 1941

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A thermodynamic system containing a number of different gaseous components will be in chemical equilibrium when the Gibbs criterion

$$\delta U)_{S,V} \geq 0$$

is satisfied. Here U, S, and V are respectively the total internal energy, entropy, and volume of the system. When it is unnecessary to distinguish between different equilibrium conditions with respect to stability, only the equality need be considered, and the criterion may be written

$$\sum_{1}^{r} \mu_i dn_i = 0$$

μ_i represents the chemical potential of any one of the r components of the system and n_i the corresponding number of moles. The chemical potential of a component may be expressed in terms of the other properties of the component by means of the following relations:

$$\mu_i = \frac{\partial U}{\partial n_i}\Big)_{S,V,\mathbf{n}_i} = \frac{\partial H}{\partial n_i}\Big)_{S,P,\mathbf{n}_i} = \frac{\partial F}{\partial n_i}\Big)_{T,V,\mathbf{n}_i} = \frac{\partial G}{\partial n_i}\Big)_{T,P,\mathbf{n}_i}$$

where H, F, and G are respectively the total enthalpy, free energy, and free enthalpy, and the subscript $\mathbf{n}_i$ indicates that all n's are constant except n_i.

If the r components consist of a atomic species and r-a molecular constituents, formed by various combinations of these atoms, and if the total number of each kind of atom is constant, the equilibrium condition for the system becomes

$$\sigma_j(\mu) = 0 \qquad j = 1, 2, \ldots, (r\text{-}a)$$

The operator σ_j indicates a summation in which the μ for the molecule is positive, while the μ for each of the constituent atoms is multiplied by the number of atoms in the molecule and is negative. For example, the equation for H_2O would be

$$\mu_{H_2O} - 2\mu_H - \mu_O = 0$$

Expressing the chemical potentials in terms of the specific enthalpies and entropies, the equilibrium condition may finally be written

$$\Pi_j(c) = \alpha_j \qquad j = 1, 2, \ldots, (r\text{-}a)$$

Here c is the molar concentration, and α_j, the equilibrium constant for any molecular component, is a function of the temperature only.

The equation for H_2O becomes

$$\Pi_{H_2O}(c) = \frac{c_{H_2O}}{(c_H)^2 c_O} = \alpha_{H_2O}$$

The conservation of each of the atomic species provides a relations of the form

$$\Sigma a_\eta n_i = N_\eta ,$$

where a_η is the number of atoms of atomic species η in any molecule, n_i is the number of moles of that molecular component, and the summation is to include all molecules containing the given atomic species. The number of moles of each of the r-a molecules in these equations may be eliminated by means of the r-a relations of the equilibrium conditions, leaving a algebraic equations in the a atomic concentrations. The coefficients of these equations will be integral multiples of the r-a equilibrium constants, α_j, and the parameters will be the a values N_η/V. For any given temperature and set of values of the parameters, it is possible to find a unique solution of these equations.

As an example of this method of treating equilibrium gas mixtures, the hydrogen-oxygen system has been considered. The number of atomic species is 2, and the total number of components is 6, namely H, O, H_2, O_2, OH, and H_2O. From the equilibrium conditions, four relations are obtained as follows:

$$\frac{n_{H_2}}{(n_H)^2} V = \alpha_{H_2} \qquad \frac{n_{O_2}}{(n_O)^2} V = \alpha_{O_2}$$

$$\frac{n_{OH}}{(n_O)\,(n_H)} V = \alpha_{OH} \qquad \frac{n_{H_2O}}{(n_H)^2 (n_O)} V^2 = \alpha_{H_2O}$$

After the concentrations of the molecular components have been eliminated by means of these relations, the equations for the atomic summations may be written as

$$\frac{N_H}{V} = (c_H) + 2\alpha_{H_2} (c_H)^2 + \alpha_{OH}(c_O)(c_H) + 2\alpha_{H_2O}(c_H)^2 (c_O),$$

and

$$\frac{N_O}{V} = (c_O) + 2\alpha_{O_2}(c_O)^2 + \alpha_{OH}(c_O)\,(c_H) + \alpha_{H_2O}\,(c_H)^2\,(c_O)$$

For any temperature, the α_i's are at once determined, while the parameters N_H/V and N_O/V are fixed by the initial composition of the combustible mixture and the final volume. When values for c_H and c_O have been found which satisfy the two equations, the composition and all other properties of the final state of the equilibrium mixture may be computed.

Solutions for these equations for a range of compositions within the combustion limits at 2600, 2800, and 3000° K have been found. A satisfactory tabulation of these solutions, and the thermodynamic properties of the corresponding mixtures, involves the selection of suitable forms of expression for the mixture parameters and the solutions. For the region in which $2N_O > N_H$, the solutions may be written in the form log $(y_0/y - 1)$ and log $(x/x_0 - 1)$ and the parameters log (N_H/V) and log $(2N_O/N_H - 1)$ = log λ. For the region in which $N_H > 2N_O$, the corresponding forms are log $(y/y_0 - 1)$, log $(x_0/x - 1)$, log $(2N_O/V)$ and log $(N_H/2N_O - 1)$ = log μ. In these expressions, x is the concentration of atomic oxygen and y the concentration of atomic hydrogen. The subscript, 0, denotes the value for the theoretical, or stoichiometric, ratio of H_2 to O_2 in the combustible mixture, which corresponds to $N_H = 2N_O$ or $\lambda = \mu$. Logarithms of the values have been tabulated, and linear interpolation between tabular values, and between values at different temperatures, gives intermediate values of adequate accuracy.

The composition, pressure, total energy, total entropy, and values of the entropy function for the equilibrium mixtures have been calculated for all of the solutions, and tables of the logarithms of these values are also given. Linear interpolation in these tables with respect to temperature may be used, but similar interpolation with respect to the composition parameters does not yield sufficiently accurate intermediate values. Logarithmic interpolation leads to reasonably satisfactory results; but until tabular values of the properties at closer intervals are available, the most accurate results are obtained by interpolating for the solutions, and then calculating the composition and properties of the mixture.

In evaluating the thermal properties of the H-O gases, the most recent specific heat data, based on spectroscopic measurements, have been used. The formulation of the equilibrium equations for the molecules in terms of their constituent atoms requires reliable energy and entropy constants for the atomic dissociations, and only from the analysis of molecular spectra by the methods of quantum mechanics can these data be obtained.

Finally, several examples are given to demonstrate the use of the tables in the solution of combustion problems. Included among these is the calculation of the temperature of hydrogen-oxygen flames of varying initial composition.

VITA

The writer was born February 12, 1900, at Dayton, Ohio. There he received his grammar and high school education, completing the latter at Stivers High School in 1918. He was graduated with the Bachelor of Science degree in Mechanical Engineering at the Carnegie Institute of Technology in 1922.

After spending two years in industrial research, he held an appointment as Research Graduate Assistant in the Engineering Experiment Station of the University of Illinois for two years. In 1926, he received the degree of Master of Science in Mechanical Engineering from the University of Illinois.

Since that time he has been a member of the staff of the Engineering Experiment Station of the University of Illinois, having been appointed Research Assistant Professor of Mechanical Engineering in 1938. For several years, he was engaged in an experimental investigation of combustion in internal combustion engines, the results of which were presented in the following publications:

"Flame Radiation and Temperature Measurements on an Internal Combustion Engine," *Ind. and Eng. Chem.*, 24:867 (1932).

"Flame Temperature in an Internal Combustion Engine Measured by Spectral-Line Reversal," *Univ. of Ill. Eng. Exp. Sta. Bul.*, No. 262 (1933).

"Measurement of Gas Temperatures in an Internal Combustion Engine," *Trans. A.S.M.E.*, 58:195 (1936).

From 1933 until 1937 he was in charge of the Heat Treatment Laboratory in the department of Mechanical Engineering.